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Ab initio study on atomic structures and physical properties of CdSe quantum nanodots

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14. ABSTRACT
The report covers simulation studies on important physical and chemical properties of CdSe quantum nanodots. Optical absorption spectra were obtained for CdSe quantum dots, with magic number ((CdSe)13, (CdSe)19, (CdSe)33 and (CdSe)34). Effects of organic ligand binding on the stability of CdSe as well as CdSe/ZnS nanoparticles with both crystalline and fullerene-like structures were also examined. Also predicted and documented were the AIIBVI (AII=Cd, Zn; BVI=S, Se, Te) structures with same basic design feature evident in current systems namely core and shell (cage) as in the case of (CdSe)13 and (CdSe)34. In related work, structure and electronic properties of ZnO clusters with specific composition identified by mass spectrometry were examined.

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Within the tasks of project, the following results have been obtained:

The extensive calculations of optical absorption spectra for CdSe quantum dots, with magic number ($(CdSe)_{13}$, $(CdSe)_{19}$, $(CdSe)_{33}$ and $(CdSe)_{34}$), have been calculated in order to identify the highly stable observed fullerene-like structures by comparison between measured and calculated optical spectra. It has been found that the simulated spectra of fullerene-like structures are in a good agreement with experimental one which allows us to confirm the synthesis of these clusters (Figure 1).

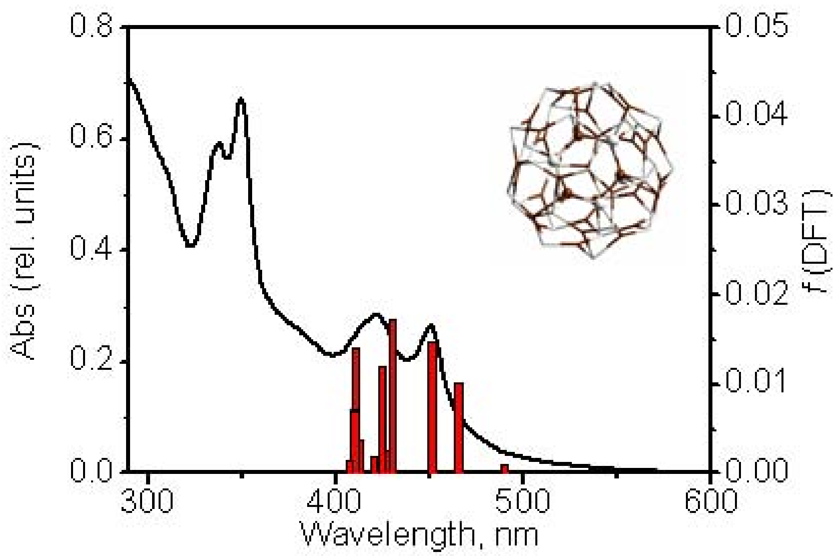

Figure 1. Spectra experiment (solid line) and calculated (red columns) for $Cd_{34}Se_{34}$.

As a continuation, we investigated the effect of organic ligand binding on the stability of CdSe as well as CdSe/ZnS nanoparticles with both crystalline and fullerene-like structures. There are several ligands, such as MAA, DTT, DHLA, employed in these calculations. The results show that the interactions of these ligands with crystalline particles are stronger than with fullerene-like particles due to charge transfer between the organic ligand and the metal surface atoms. This leads to a strong distortion of the core surface and in some cases, to decomposition of the crystalline nanoparticle. Moreover, the full covering of QDs can be easily achieved in the case of nanoparticles in

comparison to the crystalline forms (Figure 2). Our results indicate that decreasing the size of the imaging agent can possibly lead to biologically inert coverings, making it possible to avoid cellular toxicity.

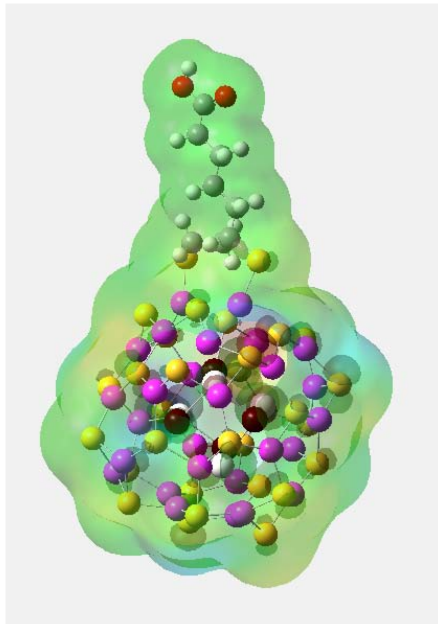

Figure 2. Diagram of covered nanodots.

We also predicted the $A_{II}B_{VI}$ (A_{II}=Cd, Zn; B_{VI}=S, Se, Te) structures with same basic design feature evident in current systems namely core and shell (cage) as in the case of $(CdSe)_{13}$ and $(CdSe)_{34}$ [1]. The shows that nanoparticles formed in vacuum as magic numbers above are found in solution as preferentially grown species in CdSe, and possibly in other $A_{II}B_{VI}$. Based on theoretical analysis, it was suggested that the high stability of the observed magic clusters originates from their specific structure as endohedral binary fullerenes.

Using first-principles calculations, we study the structure and electronic properties of ZnO clusters with specific composition identified by mass spectrometry [2]. The spectrum clearly shows a set of magic clusters neither observed nor predicted hitherto:

$(ZnO)_{34}$, $(ZnO)_{60}$ and $(ZnO)_{78}$. It was supposed, that the magic cluster of 34 monomers has the same core-cage structure as $(CdSe)_{34}$ that found us before.

References and publications emerging from this work:

1. V. R. Romanyuk, I. M. Dmitruk, Yu. A. Barnakov, R. V. Belosludov and A. Kasuya. Ultra-Stable Nanoparticles in $A_{II}B_{VI}$ (A_{II}=Cd, Zn; B_{VI}=S, Se, Te) Compounds. Journal of Nanoscience and Nanotechnology **9** (2009) 2111-2118.

2. A. Dmytruk, I. Dmitruk, I. Blonskyy, R. V. Belosludov, Y. Kawazoe and A. Kasuya. ZnO clusters: Laser Ablation Production and Time-of-flight Mass Spectroscopic Study. Microelectronic Journal **40** (2009) 218-220.